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METHOD FOR PRODUCTION OF POLYBUTYLENE TEREPHTHALATE
[Sposob polucheniya polibutilentereftalata]

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APPLICANT	:	Scientific Plastics Research Institute of the Scientific/Production Organization "Plastmassy"
NAME OF INVENTION	:	METHOD FOR PRODUCTION OF POLYBUTYLENE TEREPHTHALATE [Sposob polucheniya polibutilentereftalata]

The invention concerns a method for producing polybutylene terephthalate (PB), which has a set of valuable properties that allow it to be used as a construction material.

There is a known method of producing polyethylene terephthalate by the reaction of dimethyl terephthalate and ethylene glycol, in which a distillation column for partial condensation of evaporating ethylene glycol and return of it to the reaction zone is connected to the top of a transesterifier via a condenser. Ethylene glycol, upon being condensed, dissolves and flow back into the zone of the reaction of the dimethyl terephthalate, which has settled on the walls of the condenser and the distillation column [1].

However, this method is not suitable for the process of transesterification of dimethyl terephthalate (DMT) with 1,4-butanediol (BD), since it does not allow a process involving the dissolution and return of subliming dimethyl terephthalate back to the reactor, because the temperature of the transesterification process is substantially lower than the boiling point of 1,4-butanediol (boiling point 229.4°C), and the vapor leaving the reactor contains a negligible quantity of 1,4-butanediol. /2*

Closest in technical nature and end result is a method of producing polybutylene terephthalate by transesterification of dimethyl terephthalate with 1,4-butanediol in the presence of a catalyst, distilling out a distillate of methanol, with subsequent polycondensation of the resulting prepolymer in the melt at a reduced pressure [2].

The process of producing polybutylene terephthalate is accomplished in a reactor that is equipped, in the transesterification step, with a distillation column situated on the cover of the reactor and a methanol condenser, while in the second stage of polycondensation it is equipped with a condenser for 1,4-butanediol and vacuum traps that are cooled with liquid nitrogen to freeze out volatile products that are formed in the synthesis process.

* [Numbers in the margin indicate pagination of the original document.]

The process of transesterification of DMT with BD is carried out at 150-200°C. Partial sublimation of DMT occurs at this temperature, and the yield of target product decreases due to losses of DMT, which contaminates the methanol that is being driven off and the BD, and also clogs the walls of pipes and the column by condensing on them. In the case of industrial use of this method it is possible for plugs to form in pipelines, which can lead to an emergency situation.

In addition, in the rectification of distillates of methanol after transesterification and of 1,4-butanediol after polycondensation, problems arise with separating pure methanol and BD, since DMT forms an azeotropic mixture with 1,4-butanediol with a DMT concentration from 0.1-0.3 wt%, which prevents separation of these mixtures. /3

The goal of this invention is an increase of the productivity of the process.

This goal is achieved by the fact that in the method of producing polybutylene terephthalate by transesterification of dimethyl terephthalate with 1,4-butanediol in the presence of a catalyst involving the driving off of a methanol distillate and subsequent polycondensation of the resulting prepolymer in the melt at reduced pressure, the methanol is driven off through an absorption column, to which 1,4-butanediol is supplied at 100-150°C up to complete dissolving of the dimethyl terephthalate entrained by the methanol, and the resulting solution is returned to the reaction zone, and the mol ratio of dimethyl terephthalate and 1,4-butanediol is 1:1.1-1.6.

In addition, the starting 1,4-butanediol can contain 20-70% 1,4-butanediol from the polycondensation reactor.

The transesterification process is carried out at 150-200°C in the presence of a catalyst in a reactor equipped with an absorption column, which can be any apparatus of absorption type in which the mixture of outgoing vapor of methanol and sublimed DMT is separated by washing with BD, which is

heated above the boiling point of methanol, preferably to 100-150°C, since below 100°C a large quantity of methanol remains in the BD, while above 150°C entrainment of DMT is possible.

It is known that losses of BD during transesterification as a result of thermal destruction increase with an increase of the BD:DMT mol ratio. In the known method [2], 1.2% of the BD is converted to tetrahydrofuran at a starting DMT:BD ratio of 1:1.4. However, the smaller the quantity of BD used, the more DMT will be sublimed. Considering these phenomena, the DMT:BD ratio is usually set in the range of 1:1.6-2.5.

This invention makes it possible to conduct the synthesis of polybutylene terephthalate at a low /4
DMT:BD mol ratio equal to 1:1.1-1.6, which provides minimum cyclization of BD to tetrahydrofuran with complete utilization of the DMT.

The technological process of producing polybutylene terephthalate consists of heating the starting components, which consist of DMT, BD and catalyst, with continuous agitation, maintaining the temperature in the reactor at 150-200°C, in which case the transesterification reaction takes place, as a result of which methanol is produced. Under the reaction conditions, partial sublimation of DMT also occurs and the DMT is carried off together with the methanol vapor.

The methanol and DMT vapor from the reactor go through a heated pipe to the lower part of the absorption column, the middle part of which is fed with BD heated to 100-150°C for irrigation. BD circulation for irrigation of the column takes place throughout the transesterification process with the help of a dispensing pump. In doing so, there is complete dissolution of the DMT in the BD, while the methanol passes through the column almost without condensation. The upper part of the column serves to separate the methanol from the BD. The methanol, collected in a receiver, does not contain DMT or BD impurities.

The BD, which contains dissolved DMT, is sent from the absorption column to the next transesterification operation as an addition to the starting BD. The process of polycondensation of the prepolymer is conducted at 245-250°C under a vacuum with residual pressure of 0.5-5 mmHg, in which case the excess BD is driven off and can be returned to the next step as recycled BD.

Any of the transesterification catalysts that are known in the synthesis of polyesters can be used as catalysts: organic titanium or aluminum compounds, etc.

Example 1 /5

7760 g DMT and 5760 g BD are charged into a 25-liter apparatus, and 3.88 g tetrabutyl titanate are added as catalyst. 1440 g BD heated to 100°C circulate through an absorption column. Transesterification is carried out with a gradual increase of temperature from 150-200°C over 60 min. The methanol that is given off passes through the absorption column, condenses in a condenser and goes to a receiver. After methanol has been driven off, the line with the absorption column is closed and then the excess BD is driven off through the condenser to the BD receiver. Precondensation is carried out with a gradual rise of temperature from 200-250°C and a decrease of pressure from atmospheric to 5 mmHg over a period of 60 min. Polycondensation is carried out at 250°C in a vacuum with residual pressure 0.5-5 mmHg for 120 min. The resulting polybutylene terephthalate is discharged from the apparatus in the form of strings that are cooled in a water bath and granulated. BD from the absorption column is used in the synthesis in accordance with Example 2.

Example 2

A solution of DMT in BD from the absorption column after conducting the preceding experiment (Example 1) is charged into a 25-liter apparatus, a mixture of consisting of 7751.5 g DMT and 4320 g

fresh BD is added to achieve a ratio of the starting components DMT:BD equal to 1:1.6, and oligobutyl titanate is added in the amount of 2.33 g as catalyst. Then the synthesis process is carried out as in Example 1.

Examples 3-5

The process of producing polybutylene terephthalate is carried out as described in Example 2, except that the starting DMT:BD ratio and the temperature in the absorption column are as indicated in the table.

Example 6

7751 g DMT, 380 g recycled BD and a solution of BD containing DMT from the absorption column, /6 which were obtained from the preceding experiment in accordance with Example 5, are charged into a 25-liter apparatus and 2860 g fresh BD is added. 290 g BD are charged into the absorption column. Then the process of synthesizing polybutylene terephthalate is carried out as in Example 1.

Example 7

7755 g DMT, 1060 g recycled BD and the solution of BD containing DMT from the absorption column that were obtained from the preceding experiment in accordance with Example 6, are charged into the apparatus and 4410 g fresh BD are added. Then the synthesis of polybutylene terephthalate is carried out as in Example 1.

The technological parameters of the transesterification process and the characteristics of the BD from the absorption column, the methanol distillate, and also the specific viscosity of the polymer are given in the table.

The proposed method of producing polybutylene terephthalate makes it possible to increase the productivity of the process because of more complete utilization of the starting products, i.e., the use of the sublimed DMT in the next operation of the transesterification; elimination of intermediate prophylactic operations of cleaning fittings, pipelines and columns to remove sublimed DMT; production of methanol distillate that is free of DMT impurities; production of BD distillate that is free of DMT impurities; use of a minimal DMT:BD ratio, at which only 0.3% of the BD cyclizes to tetrahydrofuran (compared to 1.2% of the BD being converted to tetrahydrofuran in accordance with [2]).

The properties of the polybutylene terephthalate obtained in accordance with this technical solution are at the level of the properties of PB obtained by the known methods.

The proposed method of producing polybutylene terephthalate makes it possible to increase the safety of the process and to preclude emergency situations of plugs forming in pipelines, which requires emergency shutdown of the process, mechanical cleaning or burning out of the DMT plugs, and in some cases, it is even necessary to replace sections of pipes.

Thus, this invention, in which, in the method of producing PB by transesterification of dimethyl /7
terephthalate with 1,4-butanediol in the presence of a catalyst while driving a distillate of methanol and subsequent polycondensation of the resulting prepolymer in the melt at reduced pressure, the methanol is driven off through an absorption column, to which 1,4-butanediol is supplied at 100-150°C up to complete dissolution of the dimethyl terephthalate entrained by the methanol, and the resulting solution

is returned to the reaction zone, and the mol ratio of dimethyl terephthalate and 1,4-butanediol is 1:1.1-1.6, makes it possible to increase the productivity of the process.

Table /8

Description of technological parameters of process of transesterification and the specific viscosity of the polymer

No.	Example	DMT:BD ratio	Concentration of recycled BD in starting BD	Concentration of BD from column in BD mixture	Temperature of BD in column
		mol:mol	%	%	°C
1	2	3	4	5	6
1	1	1:1.6	---	---	100
2	2	1:1.6	---	25	100
3	3	1:1.3	---	31	120
4	4	1:1.1	---	40	130
5	5	1:1.1	---	38	150
6	6	1:1.3	70	31	150
7	7	1:1.6	20	5	120
8	control example*	1:1.6	without absorption column		

* – Method reproduced in correspondence with the technical solution of [2].

(continuation of table) /9

No.	Composition of impurities of BD from column		Composition of impurities of methanol distillate		$\eta_{sp.}$**
	DMT	methanol	DMT	BD	
	%	%	%	%	
1	7	8	9	10	11
1	0.59	5	0.0	0.1	0.53
2	0.60	4.9	0.0	0.1	0.54
3	1.4	3.6	0.0	0.1	0.53
4	2.3	2.8	0.0	0.0	0.52
5	2.4	2.0	0.0	0.0	0.54
6	1.6	1.8	0.0	0.0	0.54
7	0.62	3.7	0.0	0.1	0.52
8			0.4	1.9	0.52

** – Determined in m-cresol at 20°C, concentration 0.5 mg/dL

Claims /10

1. A method of producing polybutylene terephthalate by transesterification of dimethyl terephthalate with 1,4-butanediol in the presence of a catalyst while driving off a distillate of methanol and with subsequent polycondensation of the resulting prepolymer in the melt at reduced pressure, distinguished by the fact that, with the goal of increasing the productivity of the process, the methanol is driven off

through an absorption column, to which 1,4-butanediol is supplied at 100-150°C to complete dissolving of the dimethyl terephthalate entrained by the methanol, and the resulting solution is returned to the reaction zone, and the mol ratio of dimethyl terephthalate to 1,4-butanediol is 1:1.1-1.6.

2. A method as in Claim 1, distinguished by the fact that the starting 1,4-butanediol contains 20-70% 1,4-butanediol from the polycondensation reactor.

Sources of information considered in Examiner's evaluation

1. Japanese patent No. 48-7260, Cl. 26(5), D 12, published 1973.
2. US patent No. 3635899, Cl. 260-75 M, published 1972 (prototype).